

Introduction

Micelles are a common example of nanoparticles with the crucial ability of hosting small guest molecules. Salt-induced diffusiophoresis of a micelle is the migration of a charged nanoparticle in water, induced by an imposed directional gradient of salt concentration (Fig. 1).¹ This transport phenomenon has emerged as a valuable tool for particle manipulation inside porous materials and microfluidics.^{2,3} Since diffusiophoresis depends on the intrinsic ability of micelles to randomly move (diffuse) in water, this poster show experimental micelle diffusion coefficients for the cationic surfactant, hexadecylpyridinium chloride (CPC, Fig. 2) in the presence of aqueous NaCl and KCl. The electrical double layer (EDL) theory⁴ was successfully employed to explain the effect of surfactant and salt concentrations on the observed micelle diffusion coefficient.



FIG 1. Salt-induced diffusiophoresis of micelle.

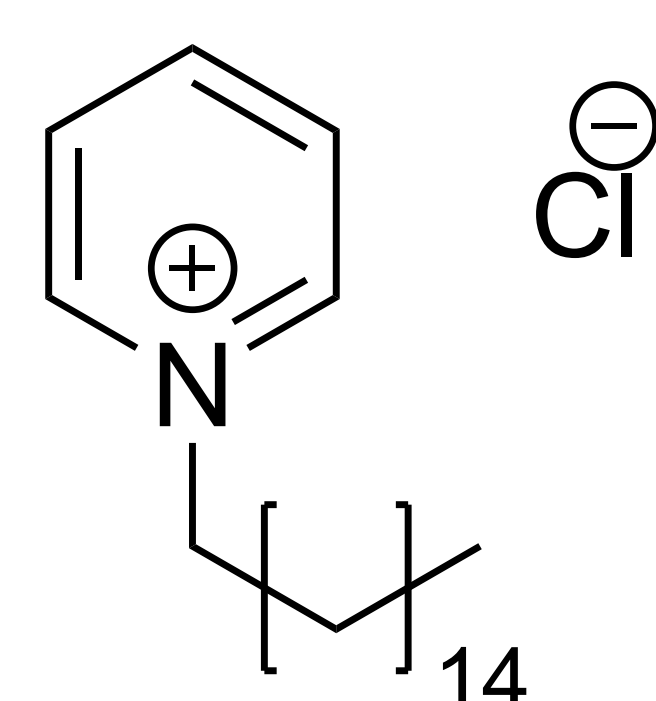


FIG 2. Chemical structure of cetylpyridinium chloride (CPC).

Method

Micelle diffusion coefficients were determined using dynamic light scattering⁵ at 25 °C.

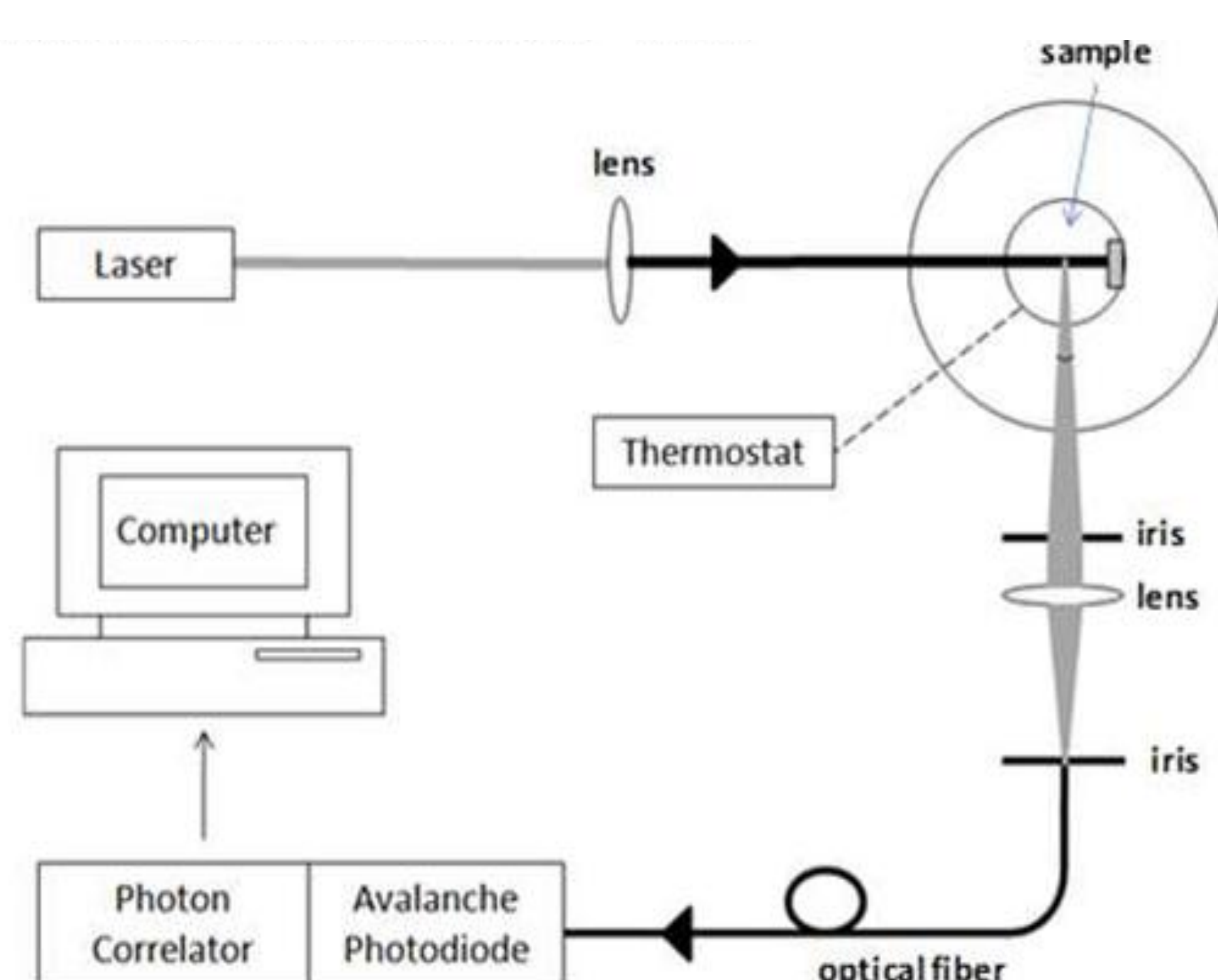


FIG 3. Scheme of Dynamic light scattering apparatus

Result and Discussion

The diffusion coefficient of CPC micelles in water was found to increase with surfactant concentration at any given salt concentration (Fig. 4).

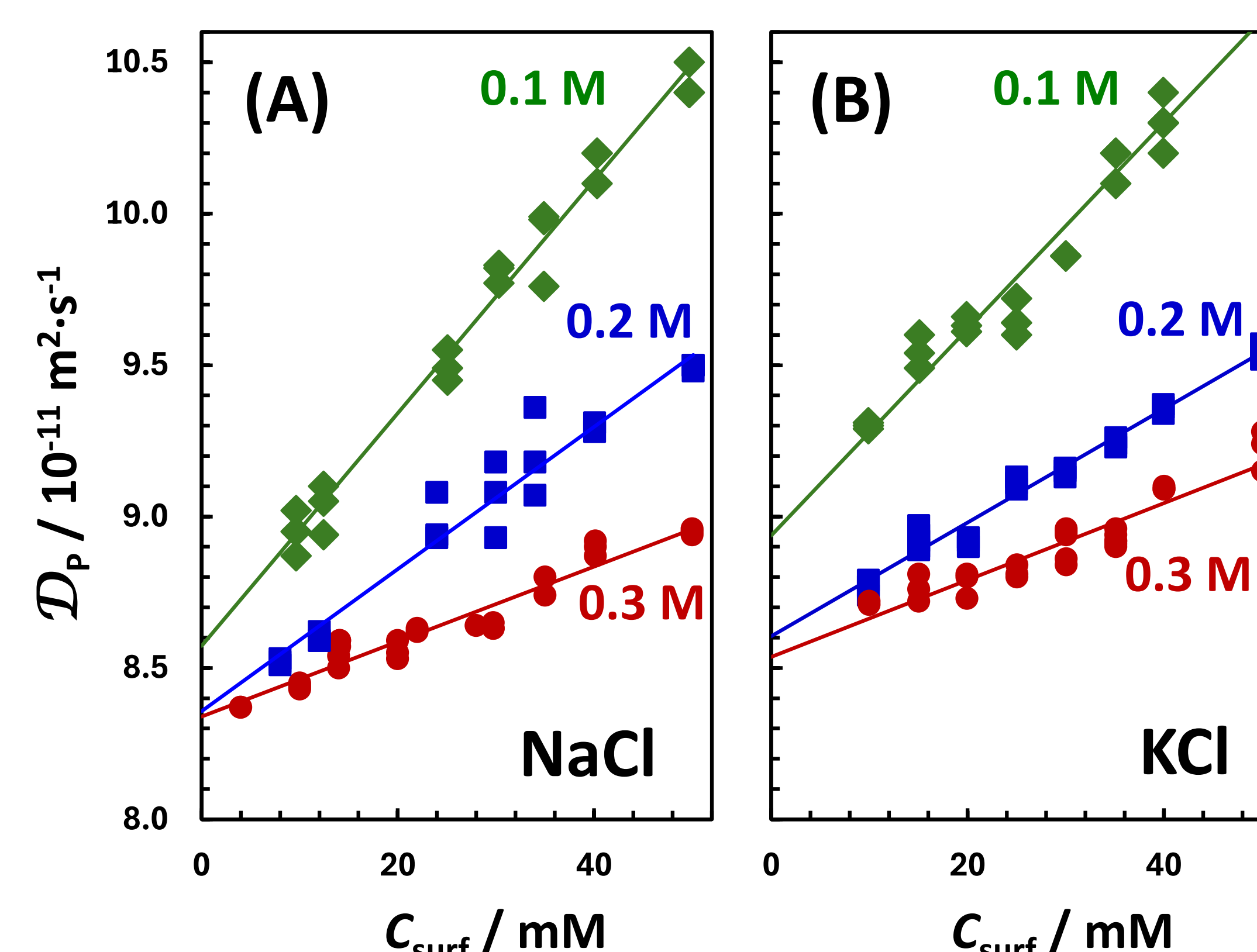


FIG 4. Diffusion coefficient of CPC micelles, D_p , as a function of CPC concentration, C_{surf} , in the presence of NaCl (A) and KCl (B). Concentration values appended to each set of data specifies salt concentration.

At each salt concentration, C_s , diffusion data were fitted using the relation:

$$D_p = D_p \cdot (1 + K \cdot C_{surf} / C_s)$$

where D_p is the micelle Brownian mobility and K is the micelle-micelle interaction parameter. D_p was used to calculate micelle radius using the Stokes-Einstein equation below, where R_p is the micelle's hydrodynamic radius, η is the viscosity of the salt-water solution, $T = 298$ K is absolute temperature and k_b is Boltzmann constant. Our results are summarized in Table 1.

$$D_p = \frac{k_b T}{6\pi\eta R_p}$$

TABLE 1. Micelle Brownian mobility, D_p , viscosity of salt-water systems, η , micelle's hydrodynamic radius, R_p , and slope, K . Values of K_{calc} are calculated using EDL theory.

C_s / M	$D_p / 10^{-11} m^2 \cdot s^{-1}$	η / cp	R_p / nm	K	K_{calc}
NaCl					
0.10	8.57±0.04	0.901	2.83±0.03	0.45 ± 0.02	0.50
0.20	8.36±0.04	0.908	2.88±0.03	0.56 ± 0.03	0.49
0.30	8.34±0.02	0.916	2.86±0.02	0.45 ± 0.03	0.48
KCl					
0.10	8.94±0.04	0.890	2.74±0.03	0.38 ± 0.02	0.50
0.20	8.60±0.02	0.889	2.84±0.03	0.44 ± 0.02	0.49
0.30	8.44±0.03	0.889	2.86±0.03	0.45 ± 0.04	0.48

Electrical Double layer theory (EDL)

Poisson Equation: $\frac{1}{r} \frac{d^2 r \psi}{dr^2} = -\frac{\rho_e}{\epsilon_0 \epsilon_r}$

r : distance from micelle center
 $\psi(r)$: electrostatic potential
 ϵ_0 : vacuum permittivity
 ϵ_r : solvent dielectric constant
 $\rho_e(r) = (\rho_M - \rho_C) \cdot e$
 $\rho_M(r) = C_s \cdot \exp(+e\psi/k_b T)$: density of coion (+)
 $\rho_C(r) = C_s \cdot \exp(-e\psi/k_b T)$: density of counterion (-)
 e : elementary electrical charge

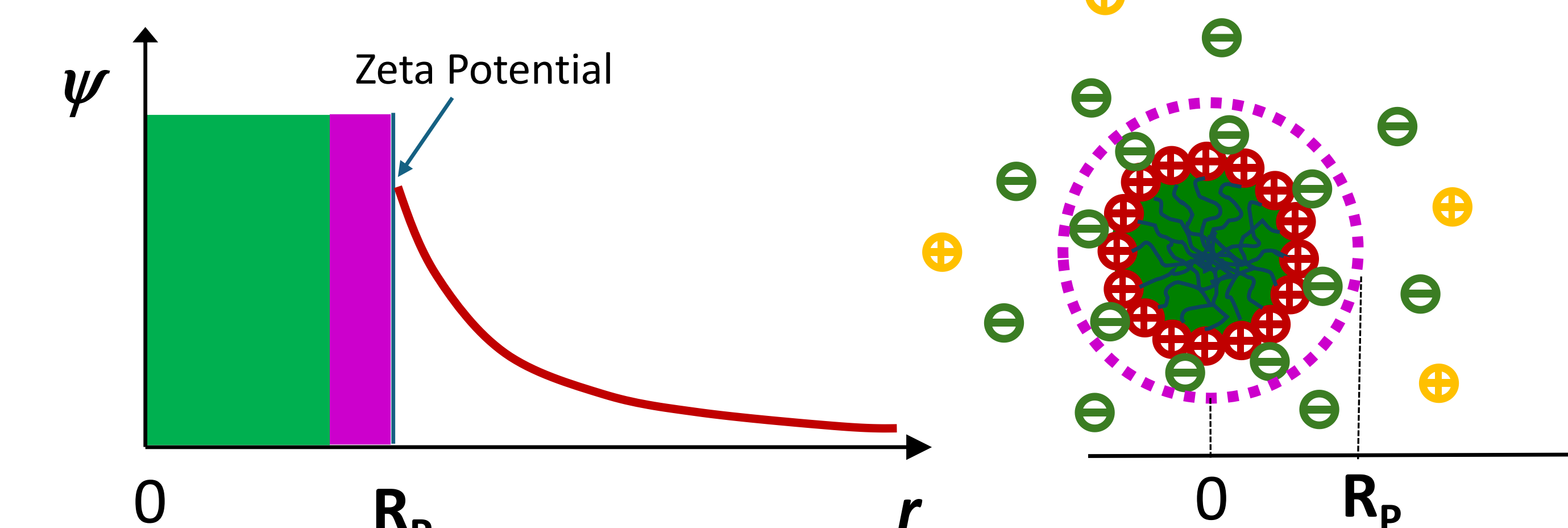


FIG 5. Electrostatic potential, ψ , as a function of radial distance from micelle center, r . Value of ψ at $r=R_p$ is zeta potential.⁴ The zeta potential was obtained by applying electroneutrality condition with micelle charge ($=+33$).

Conclusion

Micelle hydrodynamic radius, R_p , was found to be essentially independent of salt type and concentration (2.8 nm).

The slope parameter, K , was described using EDL theory. The calculated K_{calc} is in good agreement with experimental values. This implies that micelle-micelle interactions are mostly electrostatic.

The Brownian mobilities, D_p , were used to describe micelle diffusiophoresis. Please see Josie Nguyen's poster on micelle diffusiophoresis for more details.

References

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